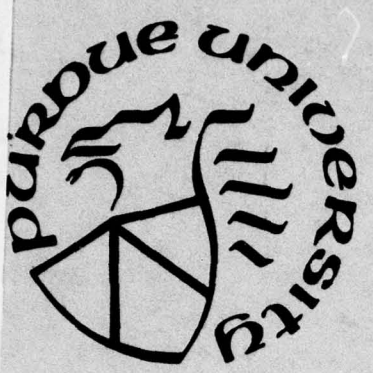
AD-A048 890 PURDUE RESEARCH FOUNDATION LAFAYETTE IND F/G 9/1
THE EFFECTS OF SUBSTRATE COMPOSITION ON THICK FILM CIRCUIT RELI--ETC(U)
NOV 77 R W VEST N00019-77-C-0327
UNCLASSIFIED NL

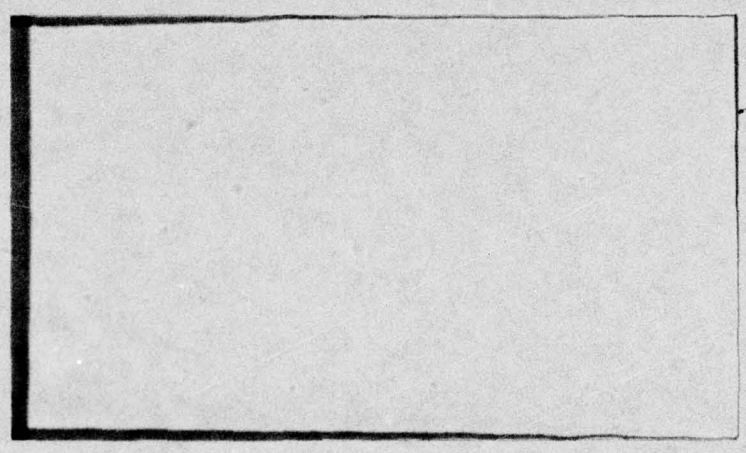
1 OF 1
ADA048 890

END
DATE FILMED
2-78
DDC



PURDUE UNIVERSITY

West Lafayette, Indiana



SCHOOL OF MATERIALS ENGINEERING

THE EFFECTS OF SUBSTRATE COMPOSITION ON THICK FILM CIRCUIT RELIABILITY

R. W. Vest

30 November 1977

Quarterly Report No. 3

For the period 8/1/77 - 10/31/77

Contract No. N00019-77-C-0327

Prepared for

NAVAL AIR SYSTEMS COMMAND

(9) Quarterly rept no. 3, 1 Aug 77-31 Oct 77

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: Three
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER

(6) 4. TITLE (and Subtitle): THE EFFECTS OF SUBSTRATE COMPOSITION ON THICK FILM CIRCUIT RELIABILITY.

5. TYPE OF REPORT & PERIOD COVERED: Quarterly Report 8/1/77 - 10/31/77

6. PERFORMING ORG. REPORT NUMBER

(10) 7. AUTHOR(s): R. W. Vest

(15) 8. CONTRACT OR GRANT NUMBER(s): N00019-77-C-0327

9. PERFORMING ORGANIZATION NAME AND ADDRESS
PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY
West Lafayette, Indiana 47907

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

(11) 11. CONTROLLING OFFICE NAME AND ADDRESS
NAVAL AIR SYSTEMS COMMAND, AIR 310B
Washington, D. C. 20361

12. REPORT DATE: 30 Nov 1977

13. NUMBER OF PAGES: 23

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

(12) 15. SECURITY CLASS. (of this report): 28 p.

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: N/A

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Thick Film Resistors
Ceramic Substrates
Electrical Resistivity
Temperature Coefficient Resistivity
Electronic Glass
Glass Sintering

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The initial stage sintering kinetics for lead borosilicate glasses were studied in order to determine the effect of substrate dissolution in the glass on the surface tension to viscosity ratio. Substrate additions up to 10 weight percent decreased the magnitude of this ratio by a factor of 10 but left its temperature dependence unchanged. Thick film resistors were fabricated with and without substrate dissolved in the resistor glass, and differences up to a factor of 100 were found in both the magnitude and temperature dependence of the sheet resistance.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601 |

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

291 600

FORWARD

Research described in this report constitutes the third three months of effort under Contract No. N00019-77-C-0327 with the Naval Air Systems Command, Department of the Navy, under the technical cognizance of James Willis. The research was conducted in the Turner Laboratory for Electroceramics, School of Materials Engineering and School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907, under the direction of Professor R. W. Vest. Contributing to the project were Messrs. J. M. Himelick, P. Palanisamy and R. L. Reed.

TABLE OF CONTENTS

I. INTRODUCTION

The print and fire processing of thick film circuits ensures that there always will be some degree of chemical interaction between the film and the substrate, because all common substrate materials are soluble to some degree in the glasses used in thick film inks. This interaction is primarily responsible for the development of adhesion between the thick film and the substrate, but it also leads to changes in the composition of the glass with the net result that the physical properties of the glass will change. These changes in physical properties of the glass will result in modified kinetics for the various microstructure development processes and all electrical properties of the resistors are related to the microstructure.

The goal of this research program is to develop a sufficient level of understanding of the phenomena involved so that appropriate models can be developed. These models should lead to the writing of specifications for impurity limits and additive ranges for substrates, and to recommendations concerning glass composition and processing conditions. Previously reported studies [1] under this program have shown that the rate of dissolution of 96% Al_2O_3 substrates (AlSiMag 614) in a lead borosilicate glass was limited by the phase boundary reaction at times important to thick film resistor processing. Rate equations were developed to allow the prediction of the total quantity of substrate dissolved in the resistor glass under any processing conditions. Standard processing (800°C, 10 minutes) will result in a fired resistor volume containing up to 20% of ingredients derived

from the substrate. Studies of the distribution of the substrate ingredients throughout the resistor glass at 800°C produced results consistent with a step change in concentration at the substrate resistor interface. Dissolution rate studies with 99.5% Al_2O_3 substrates (AlSiMag 772) showed similar results and were consistent with the proposed rate limiting step. The presence of substrate constituents dissolved in the glass were shown to have a significant effect on the temperature coefficient of resistance (TCR) of RuO_2-glass composites. A low TCR characteristic of reliable thick film resistors cannot be achieved with the model system unless an appreciable amount of substrate material is dissolved in the resistor glass.

2. GLASS SINTERING STUDIES

The surface tension and viscosity of the glass used in thick film resistors are the two properties which most strongly influence the kinetics of microstructure development and hence the final electrical behavior. In order to predict the influence of resistor-substrate interactions on the electrical parameters critical in reliability considerations, it is necessary to know how the surface tension and viscosity of the resistor glass vary with composition as more substrate is dissolved. Studies of the kinetics of initial stage sintering will yield the ratio of surface tension to viscosity, as described in a previous report [2]. Studies reported in the previous quarterly report [3] showed that the surface tension to viscosity ratio differed by a factor of more than 10 for the two base glasses (63 wt% PbO with 25 wt% B_2O_3, 12 wt% SiO_2 and 70 wt% PbO, 20 wt% B_2O_3 and 10 wt% SiO_2). It was also reported that differences in the surface tension to viscosity ratio for the same composition glass measured at different times were outside of the anticipated experimental error, and it was suspected that part of this difference was due to variations in the partial pressure of water vapor in the atmosphere of the sintering furnace. The effect of relative humidity on sintering kinetics was studied during this quarter as was the effect of substrate dissolution in the 63-25-12 glass.

2.1 Experimental

As previously discussed [1], the 63-25-12 glass composition lies very close to a two liquid phase region of the PbO-B_2O_3-SiO_2 phase

diagram, and it is difficult to obtain a homogeneous glass melt due to large differences in densities of the two liquid phases. For this reason, a special furnace was designed and constructed so that the glass melts could be stirred at temperature in order to speed the homogenization. The furnace shown schematically in Fig. 1, is maintained at a constant temperature by use of a Barber Coleman 540 Series solid state controller operating from a thermocouple. The glass melt is contained in a 75 ml platinum crucible secured in a hollowed out cavity in an alumina refractory brick. The crucible assembly can be lowered quickly out of the furnace so that the melt can be fritted or poured into a mold as required.

Frits of the 63-25-12 base glass were prepared by mixing appropriate quantities of Pb_3O_4, H_3BO_3, and SiO_2 in a rolling jar, stirred at 950°C for 90 minutes to produce a homogeneous melt, and fritted in deionized water. Glasses containing varying amounts of substrate were prepared by combining appropriate amounts of the standard 63-25-12 frit with pieces of AlSiMag 614 substrates, grinding the mixtures to -80 mesh, and melting at 1050°C in the glass furnace under agitation for 90 minutes. The melts were then fritted in deionized water and spheres fabricated by the techniques previously described [2].

2.2 Results and Discussion

Neck growth measurements between spherical glass particles were carried out utilizing the hot stage video microscope as previously described [2]. In order to determine the influence of relative

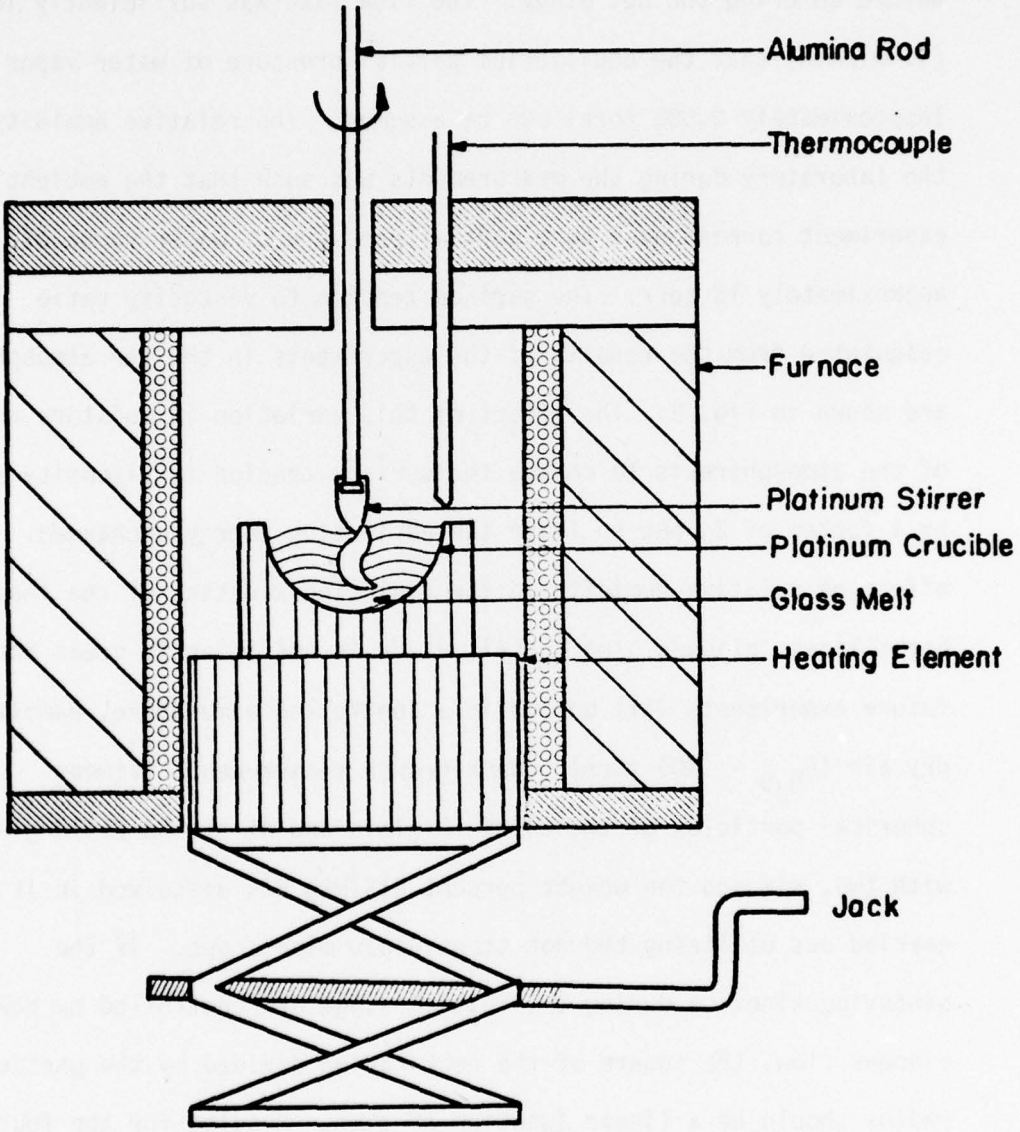


Figure 1. Glass Melting Furnace

humidity on sintering kinetics, studies were conducted with the 63-25-12 base glass in ambient air and in dry air. The dry air was produced by passing compressed air over anhydrous calcium sulfate before entering the hot stage. The flow rate was sufficiently low (15 ml/min) that the equilibrium partial pressure of water vapor (approximately 0.005 torr) can be assumed. The relative humidity in the laboratory during the measurements was such that the ambient air experiment corresponded to a partial pressure of water vapor of approximately 15 torr. The surface tension to viscosity ratio calculated from the results of the experiments in the two atmospheres are shown in Fig. 2. The effect of this variation in moisture content of the atmosphere is to change the surface tension to viscosity ratio by a factor of 2, but to leave the activation energy unchanged. This effect of relative humidity on the sintering kinetics of the lead borosilicate glasses used in this study is sufficiently great that all future experiments will be run in a controlled atmosphere, namely the dry air (P_{H_2O} = .005 torr). Neck growth measurements between spherical particles of the 63-25-12 glass and of the 63-25-12 glass with two, six and ten weight percent AlSiMag 614 dissolved in it were carried out utilizing the hot stage video microscope. If the sintering kinetics during the initial stage are controlled by Newtonian viscous flow, the square of the neck radius divided by the particle radius should be a linear function of time. Results for the four glass compositions are plotted in this way in Figs. 3-6 and the linear dependence is seen to hold quite well at all temperatures for each of the glass compositions. The proportionality constant between

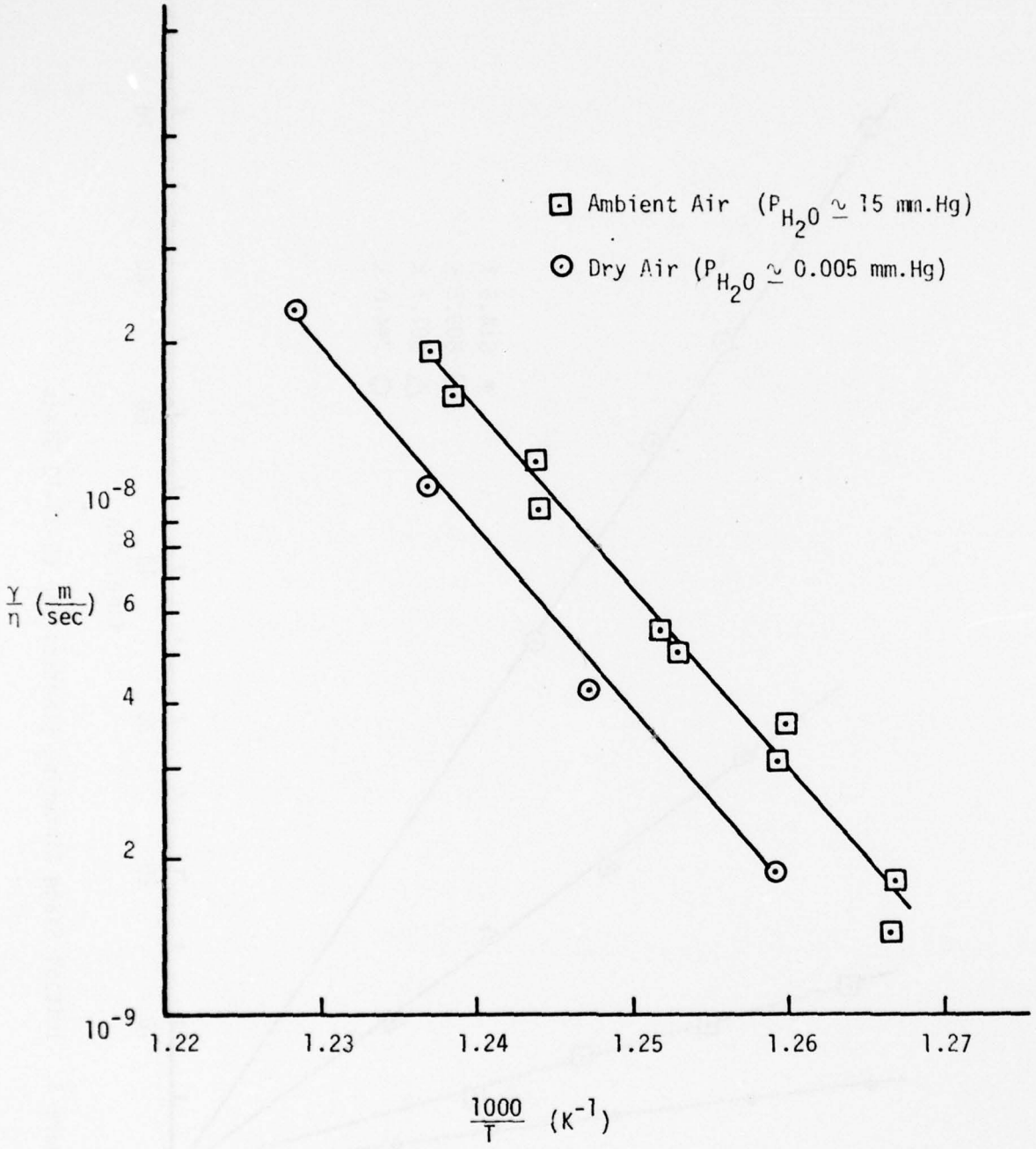


Figure 2. Effect of Relative Humidity on Surface Tension to Viscosity Ratio of 63-25-12 Glass.

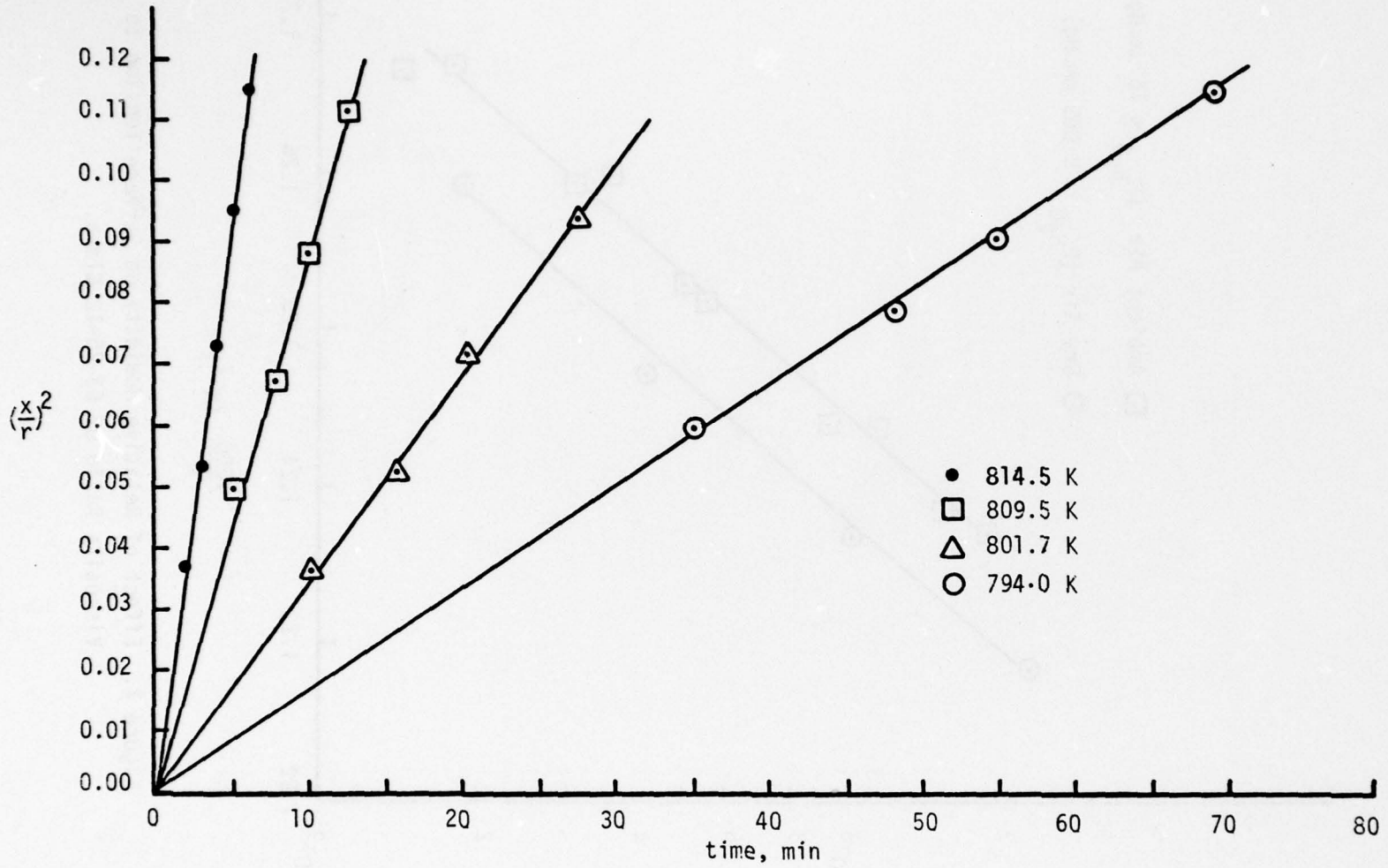


Figure 3. Initial Stage Sintering Kinetics for 63-25-12 Glass

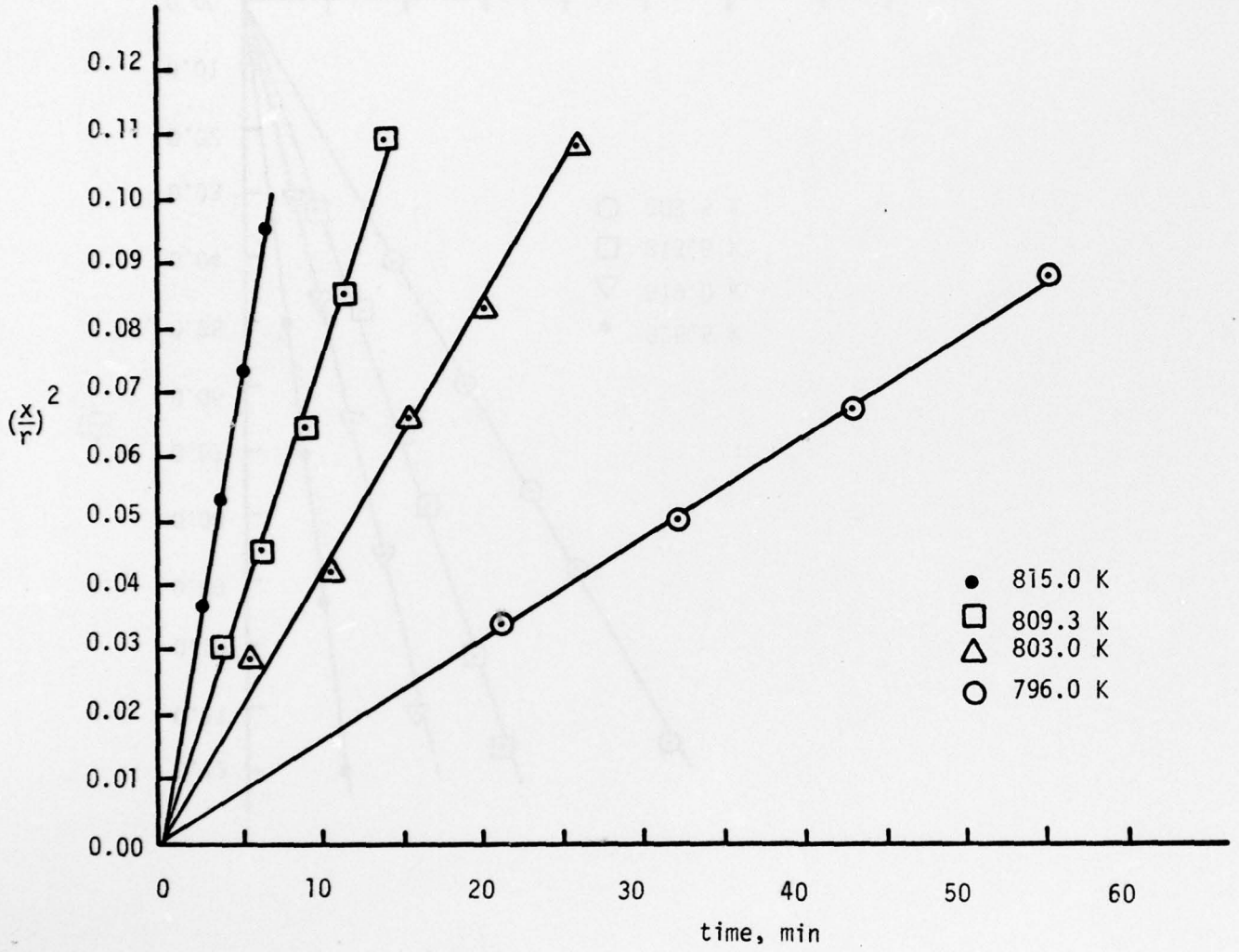


Figure 4. Initial Stage Sintering Kinetics for 63-25-12 Glass with 2 w/o AlSiMag 614

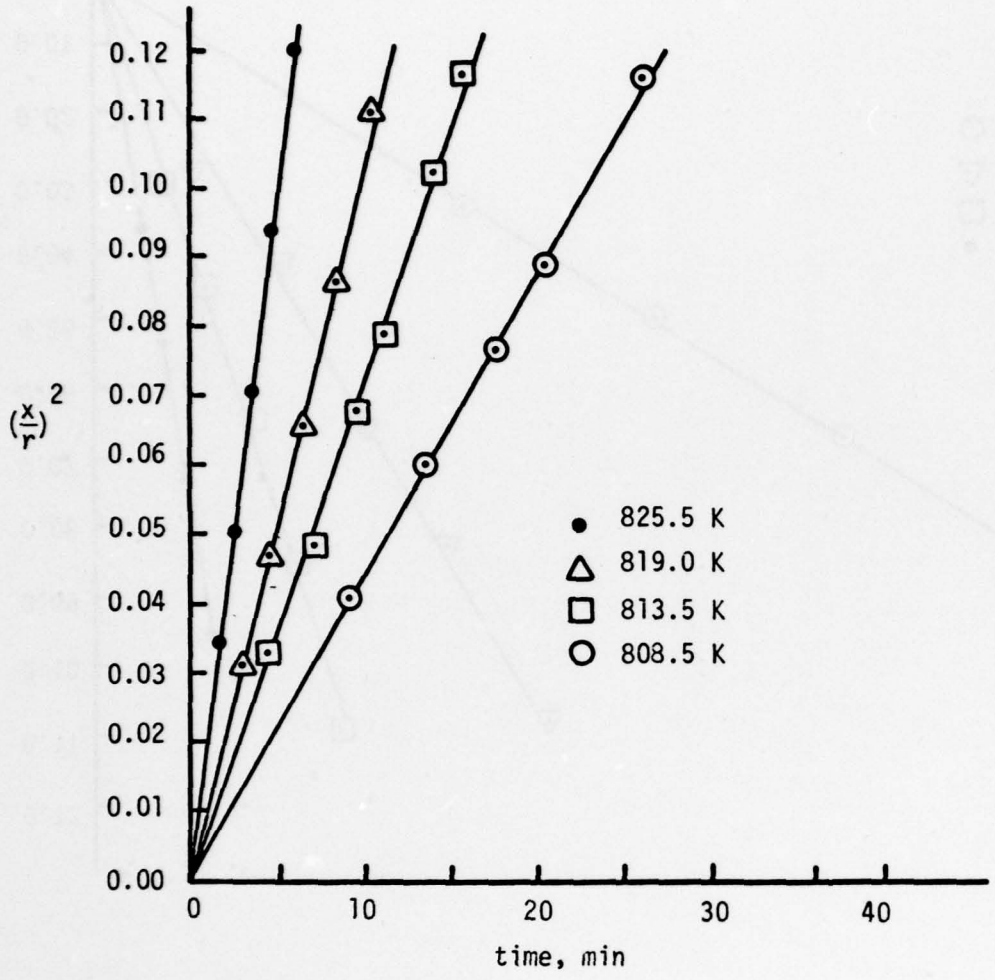


Figure 5. Initial Stage Sintering Kinetics for 63-25-12 Glass with 6 w/o AlSiMag 614

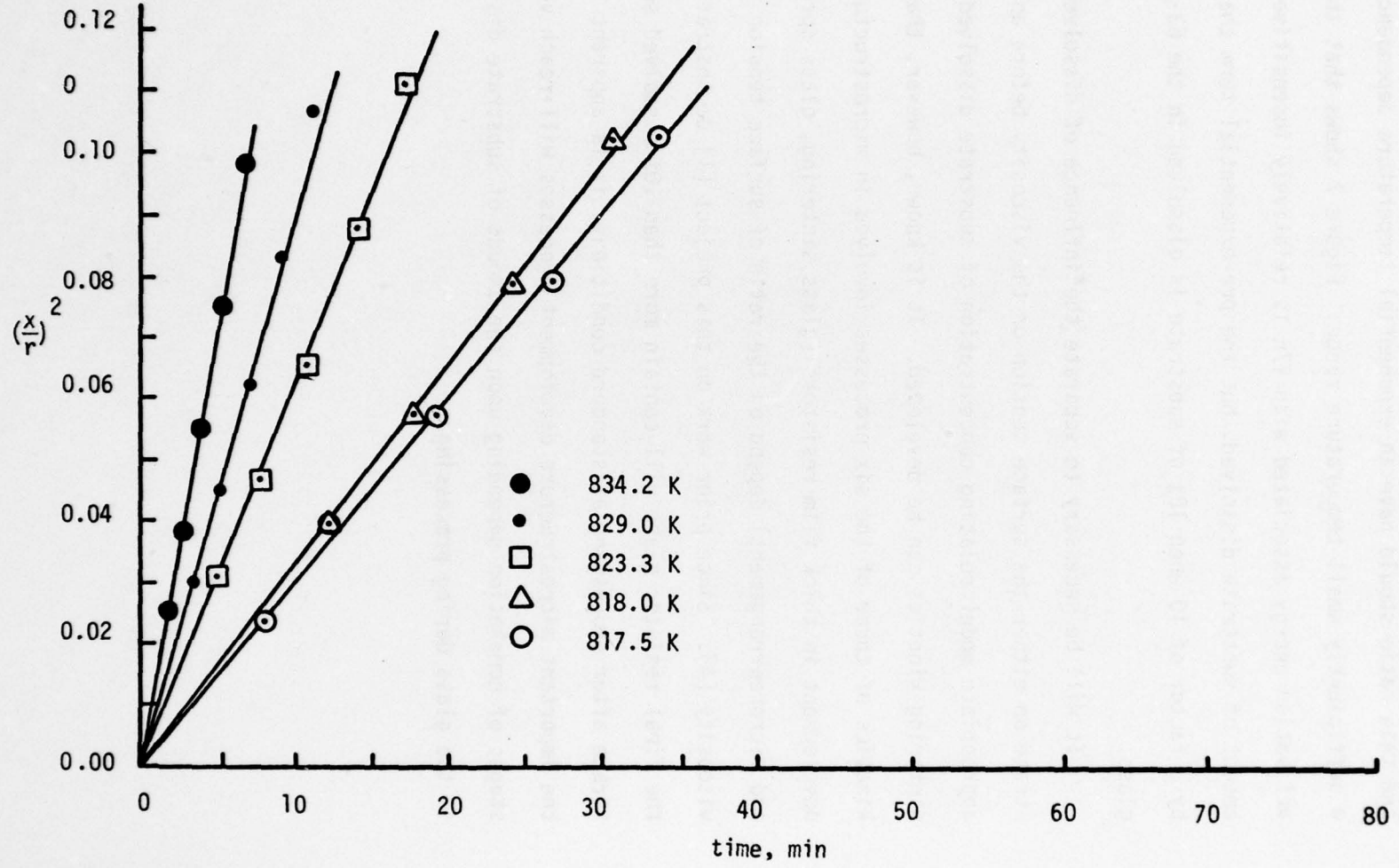


Figure 6. Initial Stage Sintering Kinetics for 63-25-12 Glass with 10 w/o AlSiMag 614

$(x/r)^2$ and time contains the ratio of surface tension to viscosity, and this ratio should have an exponential temperature dependence over a sufficiently small temperature range. Figure 7 shows that the activation energy associated with γ/η is relatively insensitive to the amount of substrate dissolved, but the pre-exponential term changes by a factor of 10 when 10% of substrate is dissolved in the 63-25-12 glass.

It will be necessary to separate the influence of dissolved substrate on either the surface tension or the viscosity before an appropriate model relating concentration of substrate dissolved and sintering kinetics can be developed. It is known, however, that the kinetics of three of the six processes involved in microstructure development in thick film resistors (glass sintering, glass spreading, and microrearrangement) depend on the ratio of surface tension to viscosity [4]. Since prior work on this project [1] demonstrated that the final resistor glass will contain more than 10% dissolved substrate after processing at standard conditions, it is apparent that the important microstructure development processes will reach varying stages of completion depending upon the amount of substrate dissolved in the glass during processing.

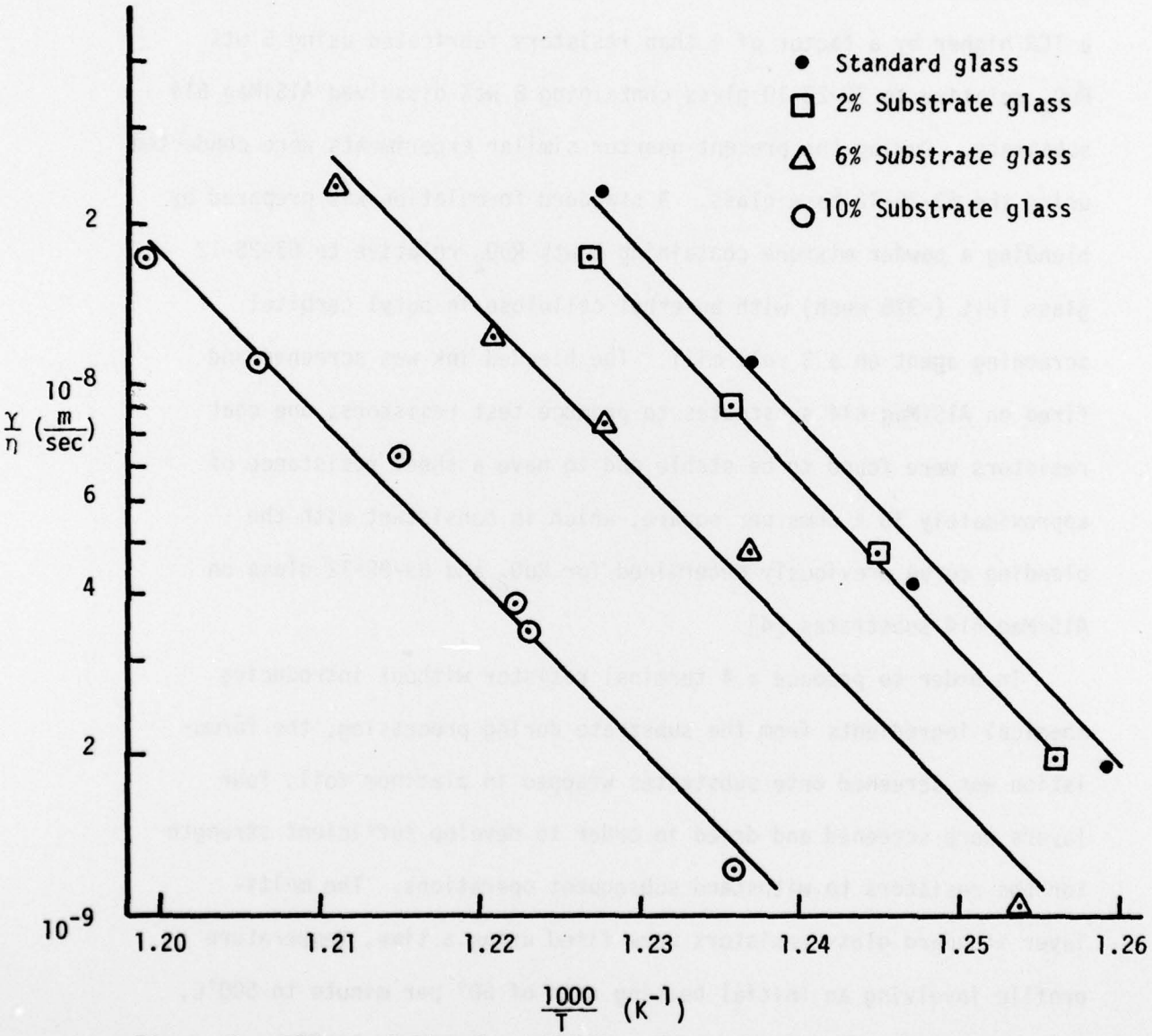


Figure 7. Effect of Dissolved AlSiMag 614 on Surface Tension to Viscosity Ratio of 63-25-12 Glass

3. ELECTRICAL PROPERTIES STUDIES

3.1 Four Terminal Resistors

In the previous report [3], it was demonstrated that resistors fabricated using 5 wt% RuO_2 relative to the 70-20-10 base glass exhibited a room temperature resistivity lower by a factor of 2 and a TCR higher by a factor of 4 than resistors fabricated using 5 wt% RuO_2 relative to 70-20-10 glass containing 8 wt% dissolved AlSiMag 614 substrate. During the present quarter similar experiments were conducted using the 63-25-12 base glass. A standard formulation was prepared by blending a powder mixture containing 5 wt% RuO_2 relative to 63-25-12 glass frit (-325 mesh) with an ethyl cellulose in butyl carbitol screening agent on a 3 roll mill. The blended ink was screened and fired on AlSiMag 614 substrates to produce test resistors; one coat resistors were found to be stable and to have a sheet resistance of approximately 35 k ohms per square, which is consistent with the blending curve previously determined for RuO_2 and 63-25-12 glass on AlSiMag 614 substrates [4].

In order to produce a 4 terminal resistor without introducing chemical ingredients from the substrate during processing, the formulation was screened onto substrates wrapped in platinum foil; four layers were screened and dried in order to develop sufficient strength for the resistors to withstand subsequent operations. The multilayer standard glass resistors were fired using a time, temperature profile involving an initial heating rate of 50° per minute to 500°C, a 10 minute hold at 500°C, a heat at 60° per minute to 800°C, a 10 minute hold, and a cool to room temperature at 160° per minute.

The fired resistors were removed from the platinum foil following the technique previously described [2]. No cracking of the resistors was observed during firing or during removal of the platinum foil. After removal from the foil the resistors must be sintered to a substrate in order to provide sufficient mechanical strength for subsequent testing, but the sintering must be carried out at a sufficiently low temperature so that no change in composition of the glass is encountered during the sintering step. Three different types of substrates were evaluated for this purpose: (1) AlSiMag 614 substrates with fired platinum electrodes; (2) AlSiMag 614 substrates pre-glazed with 63-25-12 glass; and (3) AlSiMag 614 substrates alone. Devices sintered to substrates with fired platinum electrodes were found to be unstable due to poor electrical contact at the resistor-conductive interface. Difficulties were also encountered with the stability of the devices sintered to pre-glazed substrates. It was found that sintering the resistors on plain AlSiMag 614 substrates at 520°C for 20 minutes gave stable resistors which exhibited no cracking.

A second formulation was prepared using a 63-25-12 glass in which 10 wt% AlSiMag 614 substrate had been dissolved prior to fritting. This glass was ground to -325 mesh and blended with 5 wt% RuO_2 relative to the standard glass (4.52 wt% RuO_2 relative to the glass with 10 wt% substrate dissolved). The mixed powders were then blended with ethyl cellulose in butyl carbitol screening agent on the 3 roll mill. Test resistors of this formulation printed and fired on AlSiMag 614 substrates were found to have a sheet resistance of 1.5 M ohms per square. The technique for printing and firing multi layer resistors on platinum

foil with subsequent removal of resistors from the foil was followed with this formulation. No cracking of resistors was observed during firing or during removal of the platinum foil. The 10 wt% substrate glass resistors were sintered onto glazed AlSiMag 614 substrates at 500°C for 20 minutes, and onto plain AlSiMag 614 substrates for 20 minutes at 550°C. Devices sintered on plain substrates gave the more stable devices.

Current-voltage measurements were conducted on several devices, and a linear behavior over 6 orders of magnitude using either forward or reverse polarity was observed in all cases. The data for two resistors made with standard glass and two with the 10 wt% substrate glass are shown in Fig. 8. The resistors fabricated from glass containing 10 wt% dissolved substrate showed a room temperature resistance that was higher by a factor of approximately 100 compared to the resistors fabricated with pure 63-25-12 glass. The temperature dependence of the sheet resistance relative to its value at room temperature for two standard glass resistors and two 10 wt% substrate glass resistors is shown in Fig. 9. All resistors fabricated from 10 wt% substrate glass were very stable and gave highly reproducible data over the temperature range -55° to 125°C. However, the resistors fabricated with 63-25-12 glass containing no dissolved substrate exhibited a much more erratic behavior during temperature cycling with the resistance increasing very sharply below room temperature. Curves are drawn at the low temperatures for the standard glass resistors to indicate the general behavior, but considerable variations were observed on thermal cycling and reproducible data could not be obtained.

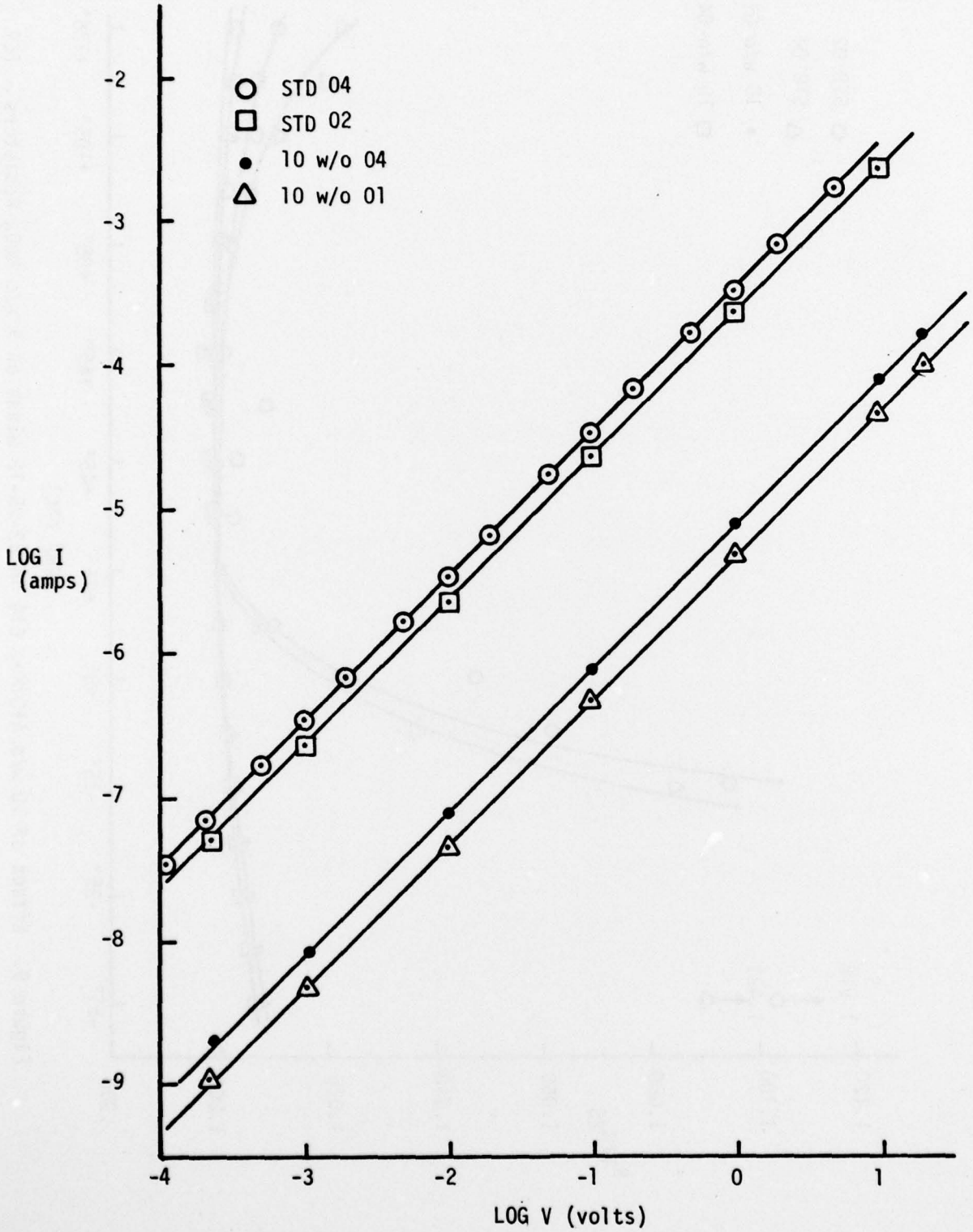


Figure 8. Effect of 10 w/o AlSiMag 614 in 63-25-12 Glass on 5 w/o RuO_2 Resistors - Sheet Resistance and VCR

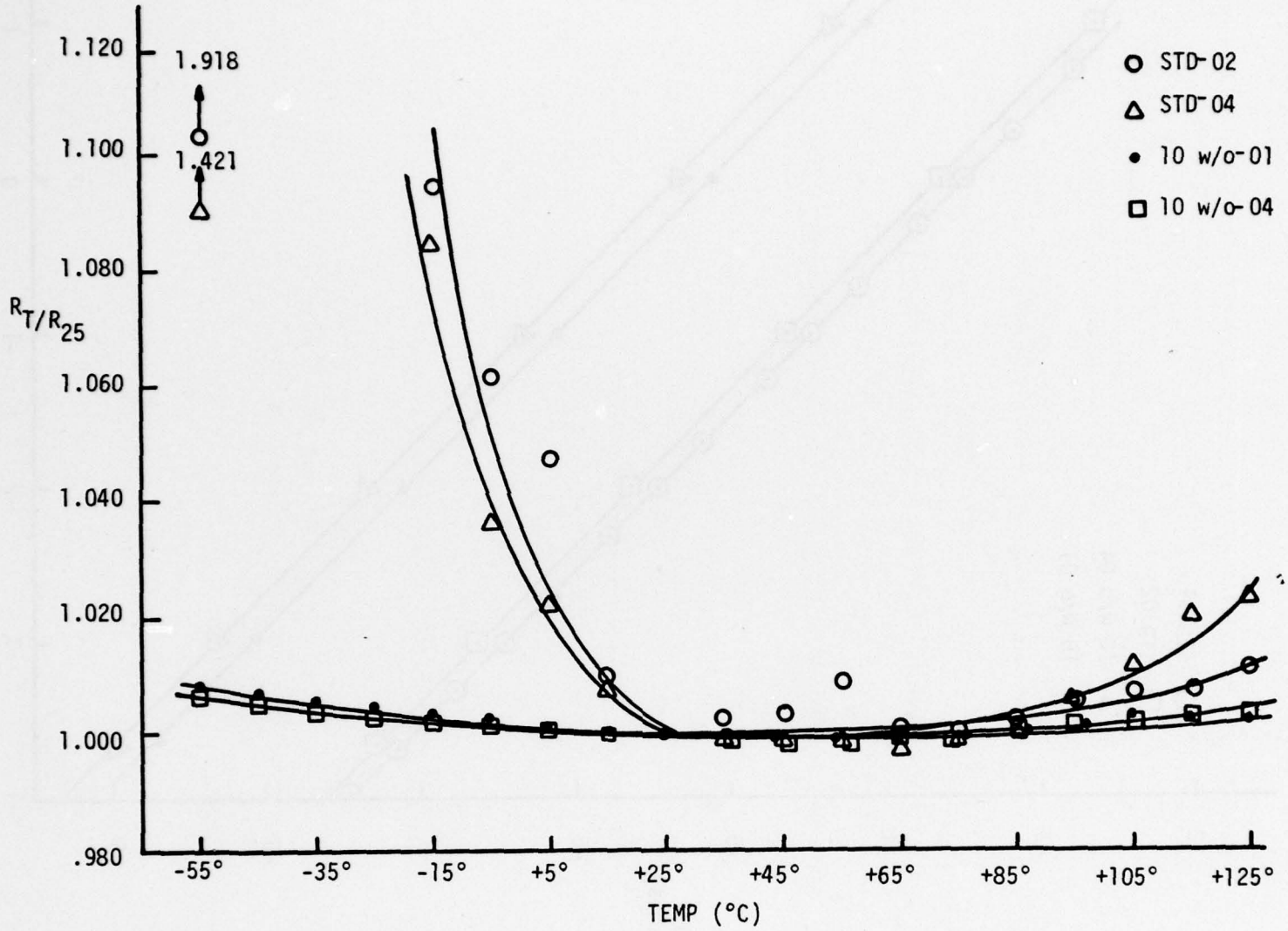


Figure 9. Effect of 10 w/o AlSiMag 614 in 63-25-12 Glass on 5 w/o RuO_2 Resistors - TCR

Representative values for hot and cold TCR for the four resistors shown in Fig. 9 are given in the following table:

Resistor No.	HOT(25°-125°C)TCR	COLD(-55°-25°C)TCR
STD-02	+120 ppm/°C	-11,500 ppm/°C
STD-04	+240 ppm/°C	-5,500 ppm/°C
10 w/o-01	+30 ppm/°C	-100 ppm/°C
10 w/o-04	+15 ppm/°C	-50 ppm/°C

The results shown in Fig. 9 and the TCR results in the preceeding table demonstrate that it is not possible to prepare a reliable thick film resistor from RuO_2 and 63-25-12 glass unless a sufficient quantity of substrate is dissolved in the glass. Previous research [4] has demonstrated that stable, high quality, low TCR resistors can be produced from a formulation containing only the 63-25-12 glass and RuO_2 when printed and fired on an AlSiMag 614 substrate, but the present results prove that the desired properties result from a partial dissolution of the substrate during processing. If a sufficient quantity of substrate is dissolved in the resistor glass prior to preparing the formulation then the desired properties, stable resistance and low TCR, can be obtained independent of the processing conditions.

3.2 MIM Devices

Progress in fabricating the desired MIM structures (Platinum-glass-platinum, platinum-glass-RuO_2, and RuO_2-glass-RuO_2) has been slowed due to difficulties in producing an adequate sputtering target

for the glass. The initial approach was to deposit a powdered glass frit by spraying or doctor blading onto aluminum targets. A low temperature sinter did not result in sufficient adhesion, and a higher temperature sinter resulted in cracking of the glass due to the severe mismatch in coefficients of thermal expansion. Techniques have now been developed for casting glass discs (13 cm diameter by 3 mm thick). These glass discs will then be cemented to the sputtering target and their sputtering behavior evaluated. The procedures for sputtering the platinum film have been developed and proven using oxidized silicon wafers as the substrates. The sputtering rates as a function of rf power have been determined and good quality films with adequate adhesion have been produced.

4. REFERENCES

1. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Final Technical Report on Contract No. N00019-76-C-0354, 28 February 1977.

2. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Contract No. N00019-77-C-0327, Quarterly Technical Report No. 1, 31 May 1977.

3. ibid, No. 2, 31 August 1977.

4. R. W. Vest, "Conduction Mechanisms in Thick Film Microcircuits," Final Technical Report, Purdue Research Foundation Grant Nos. DAHC-15-70-G7 and DAHC-15-73-G8, ARPA Order No. 1642, December 1975.

5. FUTURE PLANS

Direct measurement of the viscosity of the base glasses as a function of amount of dissolved substrate will be conducted utilizing a beam sagging technique over the same temperature range as covered in the initial stage sintering studies. These two studies will then be combined to separate the effects of composition on surface tension and on viscosity, and an appropriate model developed to describe the influence of dissolved substrate on these two physical properties of the glass. Experiments will be initiated to determine the nature of the effect of glass-substrate interactions on microstructure development by firing thick film resistors on the hot stage microscope and recording images on video tape. The glasses used will contain varying amounts of dissolved substrate ingredients. Studies of electrical properties of four terminal resistors as a function of glass composition will be extended to include measurements of current noise and short time overload. Work will continue in development of procedures for fabricating MIM structures in order to quantitatively study the electrical properties of non-sintered contacts as a function of glass composition.

6. STATEMENT OF ESTIMATED COSTS

Contract No. N00019-77-C-0327

February 1, 1977 - January 31, 1978

Beginning Fund Balance	$60,000.00
Funds Expended Through 10/31/77	39,691.71
Funds Remaining	$20,308.29

Planned Expenditures (Approximate)

November	$6700
December	6700
January	6700